

An extended Falicov-Kimball model on a triangular lattice

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The combined effect of frustration and correlation in electrons is a matter of considerable interest of late. In this context a Falicov-Kimball model on a triangular lattice with two localized states, relevant for certain correlated systems, is considered. Making use of the local symmetries of the model, our numerical study reveals a number of orbital ordered ground states, tuned by the small changes in parameters while quantum fluctuations between the localized and extended states produce homogeneous mixed valence. The inversion symmetry of the Hamiltonian is broken by most of these ordered states leading to orbitally driven ferroelectricity. We demonstrate that there is no spontaneous symmetry breaking when the ground state is inhomogeneous. The study could be relevant for frustrated systems like GdI_2 , $NaTiO_2$ (in its low temperature C2/m phase) where two Mott localized states couple to a conduction band.

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I. INTRODUCTION

Geometric frustration in correlated systems brings about a variety of phenomena and is a major area of interest in the condensed matter community presently. Systems having two dimensional (2D) layered structure with triangular lattice (for example, transition metal dichalcogenides¹⁻³, cobaltates⁴, GdI_2 ^{5,6} and its doped variant^{7,8}, $NaTiO_2$ ^{9,10}, $NaVO_2$ ¹¹ etc.) are known to come up with a host of cooperative phenomena like valence and metal insulator transitions, charge, orbital and magnetic order, unconventional superconductivity, excitonic instability¹ and possible non-Fermi liquid states^{6,12}. These systems pose a challenge to theoretical understanding as the underlying geometric frustration of the triangular lattice, coupled with strong dynamic fluctuations, give rise to a large degeneracy at low temperatures and competing ground states close by in energy. A consequence of this is a fairly complex phase diagram⁷ and the presence of soft local modes strongly coupled to the itinerant electrons⁶.

We motivate the model by looking at two systems GdI_2 and $NaTiO_2$. Each layer of Gd ions in GdI_2 form a 2D triangular lattice. They are well separated from each other by intervening layers of large Iodine ions and do not interact significantly with each other. From recent band structure (LSDA) calculations^{5,7} it is known that three nearly degenerate, spin-polarized d -orbitals (d_{z^2} , $d_{x^2-y^2}$ and d_{xy}) cross the Fermi level. Calculations involving dynamical local correlations⁶ show that these three nearly degenerate d -orbitals further break down to two doubly degenerate ($d_{x^2-y^2}$ and d_{xy}) localized levels below and one extended (d_{z^2}) level across the Fermi level. From experimental studies⁸, it is observed that the ground state is insulating and is likely to be orbitally ordered in a three sublattice fashion at half filling (each orbital occupying one sublattice) while a small doping away from half-filling

leads to phase segregation. An effective Falicov-Kimball model¹³ of spinless Fermions with two (degenerate) localized bands and one itinerant band is proposed recently for this system⁶. It would, therefore, be interesting to look for such orbitally ordered states in this context.

The corresponding Hamiltonian, then, is

$$H = - \sum_{\langle ij \rangle} (t_{ij} + \mu \delta_{ij}) d_i^\dagger d_j + E_f \sum_{i, \alpha=1,2} (f_{i\alpha}^\dagger f_{i\alpha}) + U \sum_{i, \alpha=1,2} (f_{i\alpha}^\dagger f_{i\alpha} d_i^\dagger d_i) + U_f \sum_i (f_{i1}^\dagger f_{i1} f_{i2}^\dagger f_{i2}). \quad (1)$$

Here d_i^\dagger, d_i are, respectively, the creation and annihilation operators for electrons in the itinerant band and $f_{i\alpha}^\dagger, f_{i\alpha}$ are the same for the two localized bands at the site i . The first term in Eq.(1) is the kinetic energy of d -electrons on a triangular lattice (only nearest-neighbor hopping is considered) while the second term represents the degenerate energy levels E_f of the f_1 and f_2 electrons. The third term is the on-site Coulomb repulsion between d - and f -electrons. The last one is the local repulsion between the f -electrons.

$NaTiO_2$ is another system where the above model can be applied. It also has a layered structure with alternating NaO and TiO slabs and shows a correlation-driven metal-insulator transition¹⁰. The Ti^{3+} ions with one electron in the d -orbitals are arranged on a triangular lattice and are octahedrally coordinated to oxygen ions. In the low temperature monoclinic phase the TiO_6 octahedron gets distorted, leading to a splitting in the triply degenerate t_{2g} orbitals of Ti $3d$: two orbitals are pushed below the Fermi energy while one straddles it. Orbital order due to electronic correlations has been predicted in this system earlier¹⁰. While the absence of magnetic order renders a consideration of spin degeneracy redundant, correlations in the $3d$ band would further localize

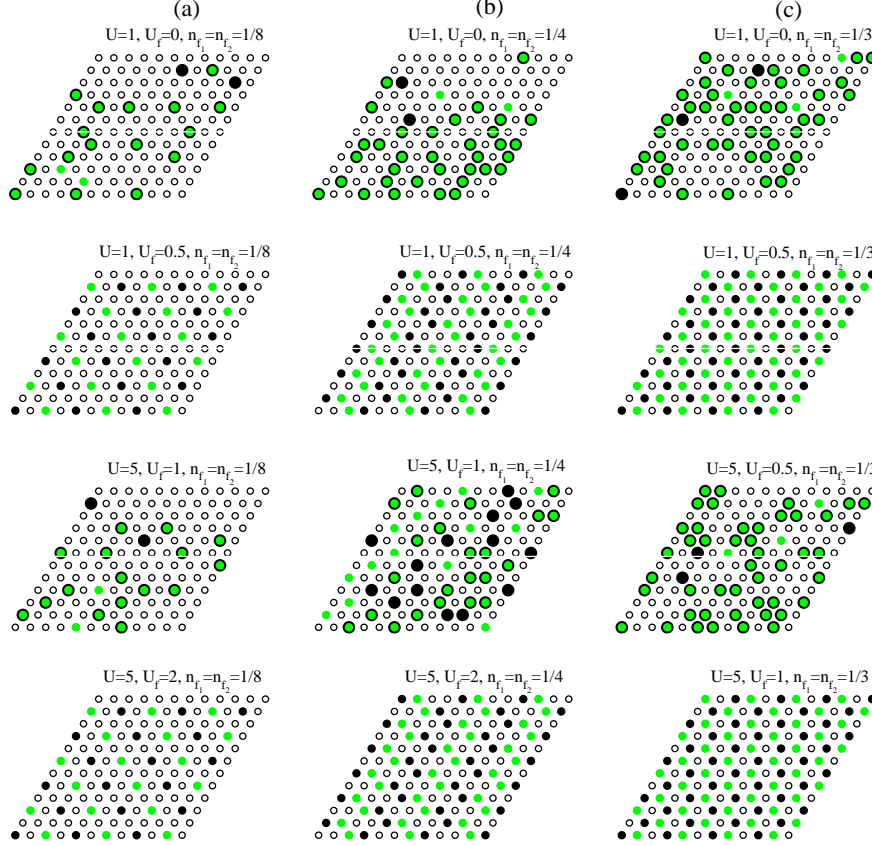


FIG. 1: (colour online) f -electron configurations are shown at each site for (a) $n_{f_1} = n_{f_2} = 1/8$, (b) $n_{f_1} = n_{f_2} = 1/4$ and (c) $n_{f_1} = n_{f_2} = 1/3$. Black and green circles correspond to sites occupied by f_1 and f_2 -electrons respectively and open circles correspond to sites with no f -electron occupancy.

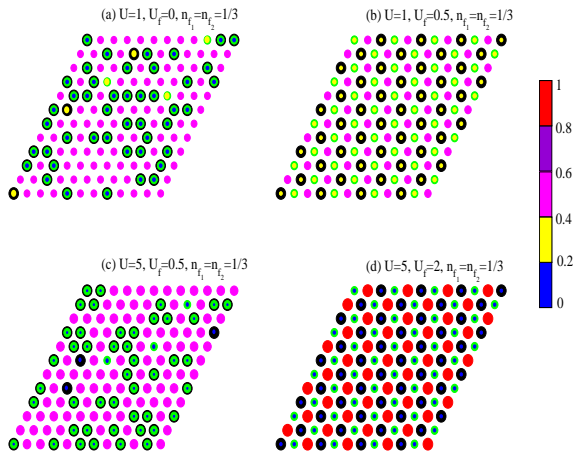


FIG. 2: (colour online) d -electron densities for different U and U_f values (set of four figures (a) to (d)) for $n_{f_1} = n_{f_2} = 1/3$.

the two bands below Fermi level and the effective model above could as well describe the low energy dynamics of this system.

The Hamiltonian conserves local f -electron occupation numbers $\hat{n}_{f,i\alpha} = f_{i\alpha}^\dagger f_{i\alpha}$ owing to the local $U(1)$ gauge invariance in the absence of f - d hybridization. Therefore, $[\hat{n}_{f,i\alpha}, H] = 0$ and $\omega_{i\alpha} = f_{i\alpha}^\dagger f_{i\alpha}$ are good quantum numbers taking values only 0 or 1. The local conservation also implies that the Hamiltonian may be written as,

$$H = \sum_{\langle ij \rangle} h_{ij}(\omega) d_i^\dagger d_j + E_f \sum_{i,\alpha} \omega_{i,\alpha} + U_f \sum_i \omega_{i1} \omega_{i2} \quad (2)$$

where $h_{ij}(\omega) = -t_{ij} + (U \sum_\alpha \omega_{i,\alpha} - \mu) \delta_{ij}$.

We set the scale of energy as the nearest neighbor hopping $t = 1$. The eigenvalue spectrum of this Hamiltonian, is easily obtained by numerical diagonalization on a finite size triangular lattice with periodic boundary condition. In order to calculate the average values of physical quantities, the classical Monte Carlo method using Metropolis algorithm can then be employed by ‘annealing’ over a subset of configurations of the ‘classical’ variables $\{\omega_{i,\alpha}\}$. This approach is known to give reliable results for the FKM, even on a triangular lattice with macroscopic degeneracies. The details of the method is reported elsewhere¹⁴.

For the systems discussed above, the number of electrons in the d -band is one at every site in the undoped limit. Therefore, in the following calculations, we restrict

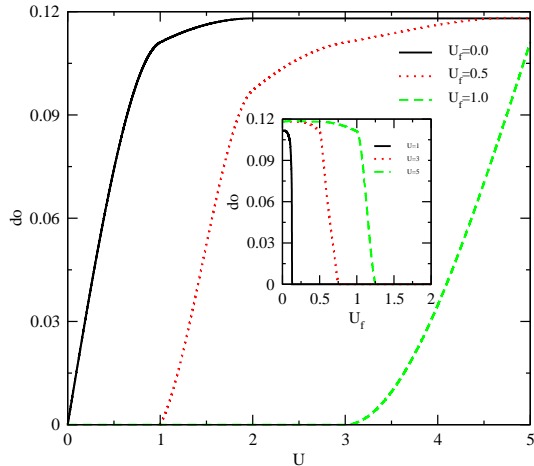


FIG. 3: (colour online) Number of sites doubly occupied by localized f -electrons versus U for different U_f (versus U_f for different U (inset)) for $n_{f_1} = n_{f_2} = 1/8$.

ourselves to the half-filled limit, i.e. $N_f + N_d = N$ where N_f , N_d and N are the total number of f -electrons, d -electrons and the number of sites in the lattice respectively (we have used $N = 144$ in all the calculations and checked a few results with larger N). In addition, $N_{f_1} = N_{f_2} = N_f/2$, as the two f -levels are degenerate.

II. RESULTS AND DISCUSSION

In Fig.1 we show the ground state configurations for different U and U_f at various f electron concentrations. Each column shows the progression of states from disorder to order to disorder and finally order again as a function of U and U_f for different n_f values. Fig.1(a) presents the case for $n_{f_1} (= \frac{N_{f_1}}{N}) = n_{f_2} = 1/8$. In the absence of any interaction between the two localized f -electron states ($U_f = 0$), no particular order is observed even on increasing the value of U . In fact, a finite U favors double occupancies of f -electrons, leaving a larger part of the lattice for d -electron motion. Therefore, with increasing U there is an increasing tendency of phase separation in real space between localized and itinerant electrons. Keeping U small (for example, $U = 1$) and making U_f finite begins to remove the local double occupancies of f electrons, reduces the overall kinetic energy of d -electrons and leads to an ordered stripe-like pattern of the two localized electrons (f_1 and f_2). This stripe pattern appears at a higher U_f when U is raised. A transition from a state of disordered doubly occupied sites to a stripe-like ordered pattern as a function of U_f at fixed U is shown in Fig.1. This is a discontinuous transition appearing at a critical value of U_f (which increases with U) and the ordered phase remains stable up to high values of U_f . Note that on raising U_f , the double occupancy is removed very quickly (see later) and the ground state

is fairly insensitive to a rise in U_f further. Similar trends are seen for other fillings too (e.g., $n_{f_1} = n_{f_2} = 1/4$ and $n_{f_1} = n_{f_2} = 1/3$, shown in Fig.1(b) and 1(c) respectively), albeit with different real space patterns of the f electrons: for $n_{f_1} = n_{f_2} = 1/4$ it is a bi-stripe orbital order whereas for $n_{f_1} = n_{f_2} = 1/3$ it is a three sub-lattice structure involving f_1 , f_2 and empty (no f -electron) sites decorating the vertices of each triangle.

One of the most interesting consequences of the various orbital orders seen in Fig.1 is that many of them break the inversion symmetry of the Hamiltonian. This will induce spontaneous displacements of the ions and the resulting lattice distortion will lead to ferroelectricity with a spontaneous finite polarisation. This is due to a specific realization of the unconventional orbital order that breaks inversion symmetry. It is driven by electronic correlation, very different from the conventional route to ferroelectricity.

In Fig.2 we present the d -electron densities at each site. It is interesting to observe how the competition among different interaction energies (such as kinetic energy of the d -electrons, on-site correlation energies between d - and f -electrons as well as between two localized f -electrons) affect the transport of the system. The d -electron density plots at each site (presented in Fig.2 for $n_{f_1} = n_{f_2} = 1/3$) clearly show the appearance of metallic and insulating and re-entrant metallic phases by tuning the parameters U and U_f . From Figs.2; (b) and (c) we see that on increasing U to a high value, keeping U_f fixed, the system goes from a stripe like ordered configuration to a phase separated state. This transition is accompanied as well by an insulator to metal transition as we discuss below. Again by keeping U fixed and increasing U_f , the ordered structure reappears and the system becomes insulating (Figs.2; (c), (d)). By tuning the interaction parameters U and U_f one can switch between these metallic and insulating states. Note that in some cases there are also sites substantially occupied by electrons of all three types (f_1 , f_2 and d). Number of sites doubly occupied by localized f -electrons predominantly plays a crucial role in determining the critical U for the metal-insulator transitions discussed above. We show the dependence of this double occupancy (do) on the interaction parameters U and U_f for $n_{f_1} = n_{f_2} = 1/8$ in Fig.3. The double occupancy do is extremely sensitive to U_f , dropping off to zero rapidly for U_f as small as 0.25 for various value of U and $n_{f,\alpha}$. It increases with U as expected and saturates quite rapidly thereafter. These features are quite general and are observed at other fillings of $n_{f,\alpha}$ also.

In order to investigate the electronic properties of these ordered phases further we have calculated the gap¹⁵ in the spectrum for each of these phases. Fig.4(a) shows the gap as a function of U_f for a series of U values, for the filling $1/8$. The disorder to order transition is indeed accompanied by a metal to insulator transition (MIT), the disordered phase has no gap at the the Fermi energy, whereas the ordered states are insulating with a

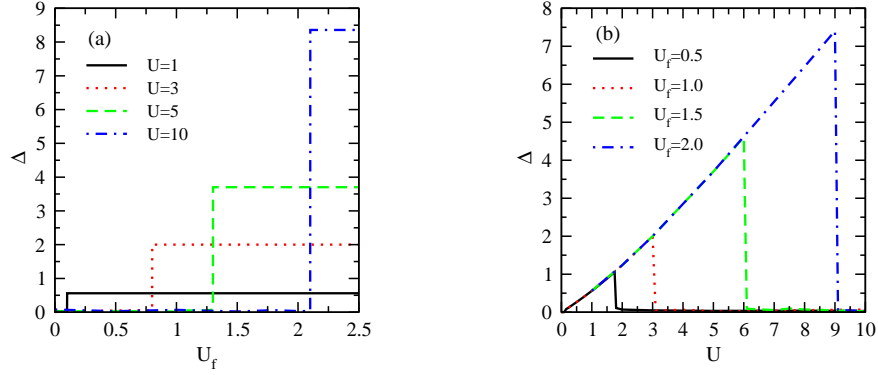


FIG. 4: (colour online) Energy gap Δ (a) as a function of U_f for different values of U (b) as a function of U for different U_f at $n_{f_1} = n_{f_2} = 1/8$.

finite gap. In addition, the gap appears at a critical U_f and remains constant beyond (independent of U_f as long as U is fixed). The discontinuous nature of the transition is clearly visible in Fig.4. On increasing U the same feature is observed, though the critical U_f for MIT increases. As U_f is the correlation energy between two localized f -electrons and U is the same between localized and itinerant electrons, there is a competition between these two interactions and therefore the critical U_f depends strongly on U . In Figs. 4(a) we show the energy gap as a function of U_f at fixed values of U for $n_{f_1} = n_{f_2} = 1/8$. An interesting observation can be gleaned from the energy gaps if we keep U_f fixed (say $U_f = 1$) and vary U . For $U = 0$ there is no gap in the spectrum and on increasing U , the gap increases almost linearly with U (Fig.4(b)). Above a certain value of U (for $U_f = 1$, at around $U = 3.2$), however, the gap suddenly drops to zero and the system becomes metallic. Therefore, as a function of U and at a fixed U_f , there is a metallic phase appearing at large U . This seemingly counter-intuitive result is understood from the fact that there are two competing processes at hand (coming from U and U_f). At $U = 0$ the d -electrons are free and the system is metallic. As U increases they avoid sites occupied by f -electrons and a gap appears. There is also a tendency towards f - d phase segregation as discussed above. A finite value of U_f , however, strongly disfavors double occupancy (as in Fig.3) and spreads the f -electrons out. Therefore, when, at a higher U , double occupancy (with f_1 and f_2 electrons) is energetically favorable over a joint occupation by f_α and d electrons at a site, the metallic state reappears. We have also calculated the corresponding density of states for different values of U and U_f showing the metallic and insulating states as discussed above (Fig.5 for $n_{f_1} = n_{f_2} = 1/3$). In Fig.6 we show the corresponding phase diagram in U - U_f plane for $n_{f_1} = n_{f_2} = 1/3$.

The presence of the local $U(1)$ gauge symmetry for each of the two localized levels have additional advantages. As the conservation of $f_{i\alpha}^\dagger f_{i\alpha}$ renders the d -electron part diagonalisable (in a ‘local’ potential

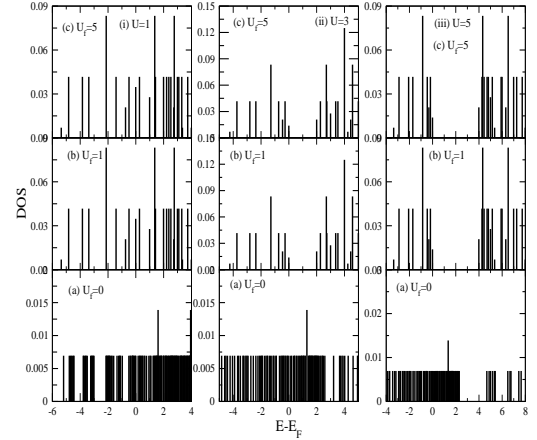


FIG. 5: Density of states for different value of U and U_f at $n_{f_1} = n_{f_2} = 1/3$.

of the f -electrons), the problem then becomes exactly solvable in the infinite dimensional limit where the d -electron self-energy is local¹⁶. Such a solution has been obtained by Brandt and Mielsch¹⁷ for the original Falicov-Kimball model. A straightforward generalization is possible in the present model as well. The local Green’s function, in the limit of infinite spatial dimension, turns out to be

$$G(\omega_n) = \langle (1 - n_{f_1})(1 - n_{f_2}) \rangle G_0(\omega_n) + \langle n_{f_1}(1 - n_{f_2}) + n_{f_2}(1 - n_{f_1}) \rangle (G_0^{-1}(\omega_n) - U)^{-1} + \langle n_{f_1}n_{f_2} \rangle (G_0^{-1}(\omega_n) - 2U)^{-1}. \quad (3)$$

where $G_0(\omega_n) = (i\omega_n + \mu + \delta(\omega_n))^{-1}$ with $\omega_n = (2n + 1)\pi KT$ the Fermionic Matsubara frequency, $\delta(\omega_n)$ the self-consistent, time-dependent generalized potential. Inserting the Dyson equation $G_0^{-1}(\omega_n) = G^{-1}(\omega_n) + \Sigma(\omega_n)$ in the above, a cubic equation for the self-energy $\Sigma(\omega_n)$ can be written. If one further takes the limit of $U_f \rightarrow \infty$, then the last term on the right side in Eqn.(3) above vanishes and writing $n_f = n_{f_1} + n_{f_2}$, one gets back the Brandt-Mielsch solution. Note that the Green’s function appears identical to that of the coherent potential ap-

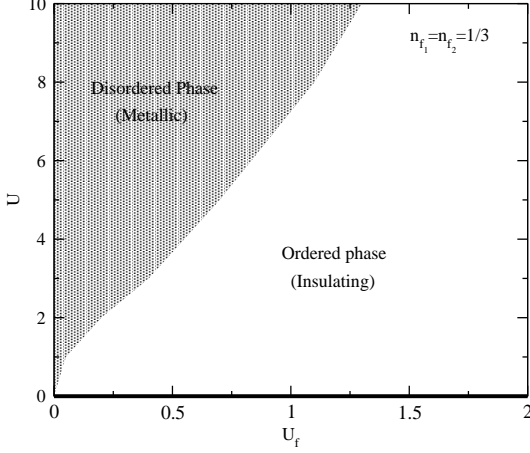


FIG. 6: Phase diagram showing metallic and insulating regions for $n_{f_1} = n_{f_2} = 1/3$, in $U - U_f$ plane. The x -axis ($U = 0$ line) is trivially metallic.

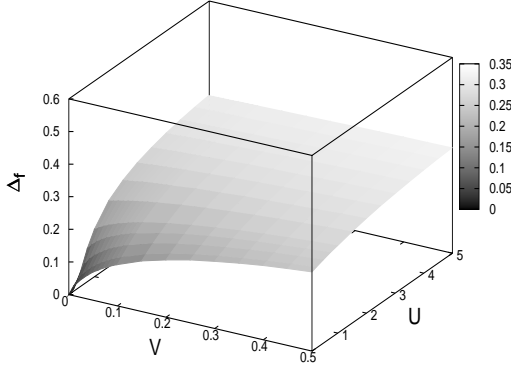


FIG. 7: The mean-field excitonic order parameter Δ_f in the V - U plane for $n_{f_1} = n_{f_2} = 1/3$.

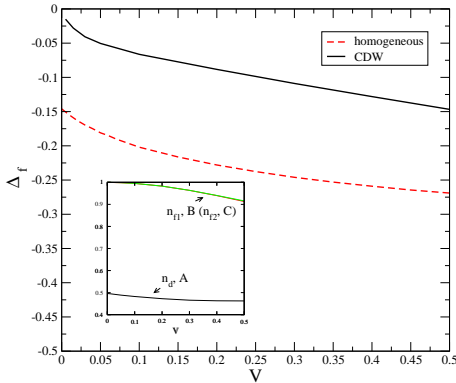


FIG. 8: (colour online) The mean-field excitonic order parameter for $n_{f_1} = n_{f_2} = 1/3$ and $U = 1$ in the homogeneous (lower curve) and ordered (upper curve) ground states. Inset shows the orbital densities at A, B and C sublattice respectively.

proximation¹⁸ (as also alloy analogy, Hubbard-III), but the difference here is that $\langle n_{f\alpha} \rangle$ are determined by the Green's function $G(\omega_n)$ through $n_f = f(\tilde{E}_{f\alpha})$ and $\tilde{E}_{f\alpha} = E_{f\alpha} - KT \sum \omega_n \log(1 - UG_0(\omega_n))$ (here $f(x)$ is the Fermi function $[1 + \exp(x - \mu)/KT]^{-1}$). In this limit, the self-energy is easily obtained in the case where the filling is $\langle n_{f_1} \rangle = \langle n_{f_2} \rangle = \langle n_d \rangle = \frac{1}{3}$. The choice of Hartree self-energy $\Sigma = U \langle n_f \rangle$ evidently minimizes the ground state energy. The corresponding configuration is an ordered three-sublattice arrangement of d , f_1 and f_2 electrons (with d , f_1 , f_2 electrons occupying A, B, C sublattices), in the limit $U_f \rightarrow \infty$ where the two types of f -electrons must not occupy the same site. In fact the argument, following Czycholl¹⁹, can be extended (for the ground state at least) to the case where a small hybridization term like $Vd_i^\dagger f_{i\alpha}$ breaks the local invariance of f_α -electron number, though the global $U(1)$ symmetry is still extant. We turn to this situation now.

There have been several studies on the FKM on a square lattice over the years with a hybridization term that mixes localized and extended electrons. An important issue in this context was raised by Portengen et al.,²⁰ regarding the spontaneous symmetry breaking (SSB) in such a model. A term $Vd_i^\dagger f_{i,\alpha}$ would induce non-zero excitonic (or ferroelectric²⁰) averages like $\langle d_i^\dagger f_{i,\alpha} \rangle$ as long as V is non zero. It was shown²⁰ from a mean-field theory calculation on a square lattice at half-filling that this average tends to a finite value even when $V \rightarrow 0$, leading to a spontaneously broken symmetry in the ground state²¹. Although the soft local dynamic fluctuations between f_α and d electrons in the limit $V \rightarrow 0$ cannot be treated properly in the static mean-field, we nevertheless undertake a similar mean-field analysis on the triangular lattice following previous work^{19,20}. Assuming a homogeneous ground state and excitonic mean-fields, we find (Fig.7) that when U is finite, averages of the type $\Delta_{f,\alpha} = \langle d_i^\dagger f_{i\alpha} \rangle$ do not vanish in the limit $V \rightarrow 0$, indicating an SSB similar to the situation on a square lattice²⁰. Such a non-zero average would, then, imply a homogeneously mixed valent ground state.

However, the assumption of a homogeneous ground state itself is called into question for the ranges of parameters being studied. It is important to note that there could possibly be other ordered states with lower energy at half-filling and one would therefore need to first ascertain the correct ground state. Czycholl¹⁹ had shown that on the square lattice, this is indeed the case and the right ground state is an ordered two-sublattice charge density state. He also showed that such a ground state does not support SSB and a homogeneous mixed valence. It is not clear a priori that on a triangular lattice, similar considerations would apply. Clearly our mean-field analysis above shows that on a homogeneous ground state, the results of Portengen et al. hold. We, therefore, look for the ground state in the mean-field theory and work out the possibility of an SSB on a triangular lattice.

Following the arguments in the infinite dimensional

limit above, we expect an ordered three-sublattice orbital density state to appear at half-filling when $n_d = n_{f,\alpha} = 1/3$ even for small finite V . We set up the mean-field calculation to look for an orbitally ordered state and allow for inhomogeneous local order parameters. This involves calculating all the local order parameters in the real space iteratively for self-consistency. We describe the result in Fig.8 where an inhomogeneous mean-field solution with a three-sublattice orbital structure emerges as the lowest energy state. The orbital density order parameter is shown in the inset of Fig.8. The A sublattice has negligible f -occupancy and a finite d -electron density, while B (C) sublattice has predominantly f_1 (f_2) occupation and a small d -occupation. Clearly as V rises, such a state becomes less stable and at a critical V the orbital order would melt (although mean-field analysis may not be quite valid in that range) due to strong quantum fluctuations. On reducing V , we observe that in the limit of $V \rightarrow 0$, the excitonic order parameter (note $\Delta_{f,\alpha} = \langle d_i^\dagger f_{i\alpha} \rangle$ is same for $\alpha = 1, 2$ in the degenerate limit considered) vanishes leading to an absence of SSB in this case. For comparison, we also show the behavior of this order parameter in a homogeneous ground state. In this case the solution supports a non-vanishing

expectation value even at $V \rightarrow 0$.

In conclusion, we have studied an extended Falikov-Kimball model with two localized states on a triangular lattice. Such a model is found to reproduce orbitally ordered insulating ground states as reported (or predicted) in experimental systems like GdI_2 ⁸, NaTiO_2 etc. Furthermore, the disorder to order transitions have also been seen to accompany a metal-insulator transition. Many of these orbitally ordered ground states would induce spontaneous lattice distortions due to the breaking of inversion symmetry and lead to ferroelectricity driven not by the conventional mechanisms, but by electronic correlations instead. We also investigate the possibility of a spontaneously broken symmetry in the form of an excitonic order parameter in this Hamiltonian and resolve that there is no SSB in the ground state on a triangular lattice.

Acknowledgments

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